

# Relaxation effects of the negative electrode TiSnSb using $^{119}\text{Sn}$ Mössbauer and $^7\text{Li}$ MAS NMR spectroscopies

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Lithium rechargeable batteries are considered the technology of choice for energy storage in portable electronic devices and zero emission vehicles. However, there are often limitations in the energy densities of the electrode materials, most commonly caused by weak capacities and limited electrode cycling life. Research is therefore underway to find new electrode materials capable of higher performance.

Conversion type materials have recently been considered as plausible alternatives to conventional electrode materials due to their large gravimetric and volumetric energy densities. The ternary alloy TiSnSb was recently proposed as a suitable negative electrode material due to its excellent electrochemical performance.<sup>1,2</sup> TiSnSb has been shown to reversibly take up more than five lithium per formula unit, leading to reversible capacities of 540 mA h/g or 4070 mA h/cm<sup>3</sup> at a rate of 2C.

During the first discharge, TiSnSb undergoes a conversion process, leading to the simultaneous formation of Li-Sb and Li-Sn intermetallic compounds. Using complementary in situ X-ray diffraction (XRD) and in situ  $^{119}\text{Sn}$  Mössbauer spectroscopy the phases Li<sub>3</sub>Sb and Li<sub>7</sub>Sn<sub>2</sub> were observed. The following electrochemical equation has been proposed for Li insertion:



However, some ambiguities remain. Two distinct resonances are observed in the  $^7\text{Li}$  solid-state NMR spectra obtained at the end of discharge. Contributions at 0, 3.5 and 8.5 ppm are tentatively assigned to the solid electrolyte interphase (SEI), Li<sub>3</sub>Sb and Li<sub>7</sub>Sn<sub>2</sub>, respectively. A second group of resonances, composed of two distinct resonances, appear at approximately 20 ppm, which are tentatively assigned to Li<sub>7</sub>Sn<sub>3</sub> (19.5 ppm) and a second Li-Sb phase (22 ppm).<sup>3</sup> It is noted that the phase Li<sub>7</sub>Sn<sub>3</sub> has not been detected via  $^{119}\text{Sn}$  Mössbauer spectroscopy during this or any previous studies of TiSnSb.

Distinct differences in chemical shift have been observed for Li<sub>3</sub>Sb produced at the end of discharge of TiSnSb versus samples of Li<sub>3</sub>Sb synthesised via solid state methods. The presence of additional elements at the end of lithiation appears to affect the chemical shift of Li<sub>3</sub>Sb. To confirm if this is the case, additional ‘model’ compounds have been studied via NMR, including TiSb<sub>2</sub> and NbSb<sub>2</sub>. Positive chemical shifts are observed for all model compounds, confirming the influence of the “inactive” elements in ternary alloys, e.g., Ti or Nb. The ternary alloy NbSnSb has also been investigated, as a direct comparison to TiSnSb, the results of which will be presented.

## References:

1. Sougrati, M. T.; Fullenwarth, J.; Debenedetti, A.; Fraise, B.; Jumas, J. C.; Monconduit, L. J. Mater. Chem. 2011, 21, 10069.
2. Marino, C.; Sougrati, M. T.; Gerke, B.; Pöttgen, R.; Huo, H.; Ménétrier, M.; Grey, C. P.; Monconduit, L. Chem. Mater. 2012, 24, 4735.
3. Bekaert, E.; Robert, F.; Lippens, P. E.; Ménétrier, M. J. Phys. Chem. C 2010, 114, 6749.

